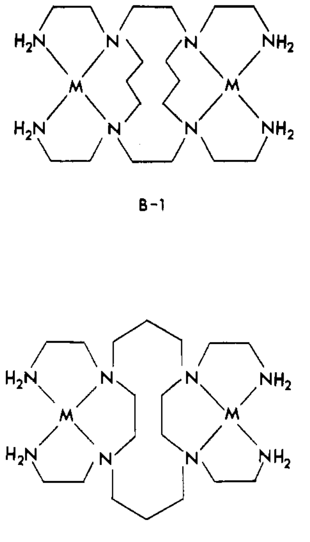


B-1

B-2

Figure 4. The two forms of dicopper(II) complex of TAEC.[7,8] The trimethylene bridges in the B-1 form completely block the space between the two metal ions, so that it is unlikely the secondary ligands will be able to bridge the gap between the two metal ions (M). There is more space in the B-2 form, which is that actually found in the monobromide complex, $[Cu_2(TAEC)Br]^{3+}$,[7,8] although bridging ligand will still be considerably sterically hindered.

2,3,2-tet stacked on different levels and held together by ethylene bridges. The B-2 form of the complex is also highly sterically crowded and is found in the monobromo complex, as indicated by X-ray crystallographic studies.[8] The level of steric crowding indicated by models for the B-2 form of $[Cu_2(TAEC)Br]^{3+}$ is such that the two coppers are not able to approach each other very closely if they lie in the plane of the four nitrogens coordinated to each of them. One must conclude that the fact that the two copper(II) ions lie[8] some 0.43 Å out of the mean plane of the nitrogen donor atoms, coupled with the unusually long Cu–Br lengths, is mainly a result of the steric crowding that prevents closer approach of the two copper(II) ions to each other. The low affinity of the $[Cu_2(TAEC)]^{4+}$ complex for hydroxide might thus have a steric component to it, with the hydroxide ion being too small to bridge the gap between the two copper(II) ions. One might have expected the binding of long ligands such as azide or thiocyanate to be relatively much higher than it is. However, structural studies show that azide binds in an end-on fashion to $[Cu_2(TAEC)]^{4+}$, with both copper(II) ions bound to the same terminal nitrogen atom of the azide ion, so that it would seem that these anions are too long to fit into the gap between the two copper(II) ions. The strong binding of secondary anions to $[Cu_2(TAEC)]^{4+}$ in spite of the considerable amount of steric strain apparently present is remarkable. The strong binding suggests that if similar systems with lower strain energy could be synthesized, very much stronger binding of secondary anions would be observed. In contrast to the TAEC analogues, models suggest that strain in the dicopper(II) complexes of BISDIEN and BISTREN is comparatively low and that there is considerable flexibility in the connecting ethereal groups bridging between the halves of the complex.

Table III shows that binding of ligands with a potential for bridging between the two copper(II) ions is usually larger than to comparable monocopper(II) complexes by about 2 orders of magnitude. One thus has a kind of "chelate effect" in reverse. Instead of the usual situation where two donor atoms that are part of a single ligand bind a single metal ion, one has here a situation where two metal ions that are part of a single complex bind a single ligand. This increase in ability to bind ligands such as bromide, which virtually do not bind to Cu(II) at all, is of considerable interest. The increased binding ability of complexes containing more than one metal ion suggests one way in which nature may be able to overcome the lack of ability to bind strongly such soft ligands by the metal ions that normally occur in biological systems.

Acknowledgment. We thank the Council Research Grants Committee of the University of the Witwatersrand, and the Foundation for Research Development, for generous financial support for this work.

Registry No. OH^-, 14280-30-9; Br^-, 24959-67-9; Cl^-, 16887-00-6; N_3^-, 14343-69-2; SCN^-, 302-04-5.

Contribution from Rocketdyne, A Division of Rockwell International,
Canoga Park, California 91303

Synthesis and Characterization of CrF_4O, $KrF_2{\cdot}CrF_4O$, and $NO^+CrF_5O^-$

Karl O. Christe,* William W. Wilson, and Roland A. Bougon†

Received January 14, 1986

Chromium(VI) tetrafluoride oxide can be prepared in high yield and purity from CrO_2F_2 and KrF_2 in HF solution. The vibrational spectra of gaseous, solid, and matrix-isolated CrF_4O and its BrF_5 and HF solutions are reported, as well as the ^{19}F NMR spectra of the BrF_5 and SO_2ClF solutions. The data confirm for gaseous, matrix-isolated, and dissolved CrF_4O a monomeric, square-pyramidal structure of symmetry C_{4v} and for solid CrF_4O a fluorine-bridged polymeric structure. CrF_4O is a strong Lewis acid, and with FNO it forms a stable $NO^+CrF_5O^-$ salt, which was characterized by vibrational spectroscopy. With KrF_2 it forms an unstable 1:1 adduct that has in the solid phase an essentially covalent structure containing a Kr–F- - -Cr bridge but is completely dissociated in SO_2ClF solution. With AsF_5 it does not form a stable adduct at temperatures as low as −78 °C, indicating that CrF_4O is a weak Lewis base. It was also shown that CrF_3O is a weak Lewis base and does not form a stable adduct at −78 °C.

Introduction

Chromium tetrafluoride oxide, CrF_4O, was first described by Edwards in 1963 as a byproduct in the direct fluorination of metallic chromium, and its unit cell dimensions were reported.[1] In 1974, Edwards and co-workers published an improved synthesis from CrO_3 and F_2 at 220 °C and gave the melting point, boiling point, vapor pressure, and description of a solid–solid transition at 24 °C.[2] Reference was made in this paper to unpublished work indicating that the low-temperature phase of CrF_4O has an endless, cis-fluorine-bridged chain structure, similar to those of MoF_4O[3] and ReF_4O.[4] The only other report on CrF_4O is a recent paper by Ogden and co-workers, who studied its infrared and UV–visible

---

† Permanent address: Centre d'Etudes Nucléaires de Saclay, IRDI/DESICP/DPC, 91191 Gif sur Yvette, France.

(1) Edwards, A. J. *Proc. Chem. Soc., London* **1963**, 205.
(2) Edwards, A. J.; Falconer, W. E.; Sunder, W. A. *J. Chem. Soc., Dalton Trans.* **1974**, 541.
(3) Edwards, A. J.; Steventon, B. R. *J. Chem. Soc. A* **1968**, 2503.
(4) Edwards, A. J.; Jones, G. R. *J. Chem. Soc. A* **1968**, 2511.

0020-1669/86/1325-2163$01.50/0 © 1986 American Chemical Society

spectra in N_2 matrices.[5] From a measurement of the chromium isotopic shifts and relative intensities they concluded that monomeric CrF_4O has a square-pyramidal structure of symmetry C_{4v} and an OCrF bond angle of about 106°. In addition, they found that CrF_4O combines with CsF and that the resulting 1:1 adduct has infrared bands at 955 cm^{-1} (ν(Cr=O)) and 650–720 cm^{-1} (ν(Cr—F)).[5] In this paper we present the results from an independent study that was undertaken in our laboratory before the paper of Ogden et al. appeared. It includes a new synthesis for CrF_4O and spectroscopic data for CrF_4O in the gas phase, in the solid state, and in different solvents. In addition, the previously reported matrix isolation data[5] were confirmed and the amphoteric nature of CrF_4O was studied.

Experimental Section

Apparatus. Volatile materials were manipulated in stainless-steel vacuum lines equipped with Teflon-FEP U-traps, 316 stainless-steel bellows-seal or Teflon-PFA (Fluoroware, Inc.) valves, and a Heise Bourdon tube-type pressure gauge.[6] Either Teflon-FEP ampules or sapphire tubes (Tyco Co.) equipped with stainless-steel or Teflon valves were used as reaction vessels. The vacuum lines and other hardware employed were passivated with ClF_3 and BrF_5 and, if HF was to be used, with HF. Nonvolatile or marginally volatile materials were handled in the dry nitrogen atmosphere of a glovebox.

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). Spectra of gases were obtained by using a Teflon cell of 5-cm path length equipped with AgCl windows. Matrix isolation spectra were obtained at 6 K with an Air Products Model DE202S helium refrigerator equipped with CsI windows. Research-grade Ne and N_2 (Matheson) were used as matrix materials in mole ratios of 400:1. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion laser or the 647.1-nm exciting line of a Kr ion laser, respectively. Sealed quartz, Teflon-FEP, and sapphire tubes were used as sample containers in the transverse-viewing–transverse-excitation mode. A previously described[7] device was used for recording the low-temperature spectra. The ^{19}F NMR spectra of the samples contained in sealed, 5 mm o.d. Teflon-FEP tubes (Wilmad Glass Co.) were recorded at 84.6 MHz on a Varian Model EM390 spectrometer equipped with a variable-temperature probe. X-ray diffraction patterns of the powdered samples in sealed 0.5-mm quartz capillaries were obtained by using a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6-mm-diameter Philips camera.

Materials. Literature methods were used for the syntheses of FNO[8] and CrO_2F_2[9] and for the drying of HF.[10] For KrF_2, the literature method involving UV photolysis of Kr and liquid F_2 in Pyrex[11] was modified by the use of a stainless-steel reactor equipped with a sapphire window.[12] AsF_5 and SO_2ClF (Ozark Mahoning) and BrF_5 (Matheson) were purified by fractional condensation prior to their use.

Synthesis of CrF_4O. Into a passivated 0.75 in. o.d. Teflon-PFA U-tube attached to two Teflon-PFA valves (Fluoroware, Inc.) was condensed a weighed amount (5.50 mmol) of KrF_2 at −78 °C under a dynamic vacuum. Then CrO_2F_2 (5.6 mmol) and dry HF (~2.3 mL of liquid) were added at −196 °C. The mixture was allowed to warm from −196 °C to ambient temperature. The resulting dark brown solution was kept at ambient temperature for 2 days until no further gas evolution was observed and the color of the solution had changed from brown to purple. The mixture was cooled to −196 °C, and oxygen (2.7 mmol) was measured. The residue was separated on warmup from −196 °C by fractional condensation under a dynamic vacuum through a series of cold traps kept at −31, −78, −126, and −210 °C. The following products were collected in these traps: −31 (CrF_4O, 5.5 mmol), −78 (small amount of CrO_2F_2), −126 (HF), −196 (Kr, 5.5 mmol). CrF_4O was characterized by its vibrational and ^{19}F NMR spectra and its melting point (55 °C) and vapor pressure.[2]

Synthesis of $NO^+CrF_5O^-$. Into a passivated 0.5 in. o.d. Teflon-FEP U-tube, attached to two Teflon valves, were condensed CrF_4O (0.957 mmol) and FNO (2.15 mmol) at −196 °C. The contents of the tube were allowed to warm to ambient temperature. At first a dark red-brown solid formed, which turned progressively lighter and finally resulted in a pink color. The material volatile at 25 °C was pumped off and consisted of FNO (1.19 mmol), leaving behind 185.3 mg (weight calculated for 0.957 mmol of $NO^+CrF_5O^-$ 184.7 mg) of a pink solid that was characterized by vibrational spectroscopy as $NO^+CrF_5O^-$ and according to its DSC analysis starts to decompose exothermically at about 237 °C. Its X-ray powder pattern showed the following *d* spacings (Å): 6.51 w, 5.94 vw, 5.12 m, 4.84 vs, 4.46 mw, 4.02 vs, 3.89 vw, 3.342 vs, 3.005 mw, 2.882 m, 2.231 ms, 2.015 w, 1.992 w, 1.949 w, 1.914 vw, 1.845 w, 1.799 w, 1.770 w, 1.717 w, 1.677 w, 1.586 w, 1.511 vw, 1.453 vw, 1.426 vw, 1.409 vw.

The CrF_4O–AsF_5 System. Into a 0.5 in. o.d. sapphire tube, capped off by a Teflon valve, were condensed CrF_4O (0.370 mmol) and AsF_5 (0.515 mmol) at −196 °C. The temperature of the mixture was cycled several times between −196 and 25 °C. In contrast with pure CrF_4O, which exhibits a purple color in the gas phase, the gaseous AsF_5–CrF_4O mixture did not show any detectable color at 25 °C and the color of the solid in the bottom of the tube had changed from the dark purple of CrF_4O to a red-brown. The mixture was cooled to −78 °C, and the volatile material was pumped off. It consisted of AsF_5 (0.50 mmol). The residue, nonvolatile at −78 °C, consisted of CrF_4O (0.37 mmol), indicating that CrF_4O does not form a stable adduct with AsF_5 at temperatures as low as −78 °C.

The CrF_3O–AsF_5 System. When CrF_3O (obtained from the reaction of CrF_4O–HF mixtures in stainless-steel equipment) was treated with an excess of AsF_5, as described above for the CrF_4O–AsF_5 system, all the AsF_5 starting material was quantitatively recovered by pumping on the mixture at −78 °C.

Results and Discussion

CrF_4O. Synthesis. The reaction of CrO_2F_2 with KrF_2 in anhydrous HF solution at room temperature provides a new synthesis for CrF_4O. The reaction proceeds quantitatively according to

$$2CrO_2F_2 + 2KrF_2 \xrightarrow[20\ °C]{HF} 2CrF_4O + 2Kr + O_2$$

The reaction is initially slow, as can be judged from the color of the HF solution, but once started it proceeds faster. The use of steel equipment should be avoided for this reaction because a mixture of HF and CrF_4O rapidly attacks steel with formation of CrF_3O.

The use of a twofold excess of KrF_2 in the above reaction did not result in additional oxygen–fluorine exchange and concomitant CrF_6 formation. Instead, the formation of an unstable 1:1 adduct between CrF_4O and KrF_2 was observed. When it was warmed to room temperature, the KrF_2·CrF_4O adduct slowly decomposed with Kr, F_2, and CrF_4O evolution. The nature of the adduct was studied and will be discussed below. In view of the tendency of CrF_4O to form an adduct with an excess of KrF_2 and the relative ease of separating CrF_4O from CrO_2F_2 by fractional condensation using trapping temperatures of −31 °C (bromobenzene slush bath) for CrF_4O and −78 °C for CrO_2F_2, the use of a slight excess of CrO_2F_2 is preferable for the synthesis of CrF_4O.

The previously reported method[2,5] for the synthesis of CrF_4O involved the fluorination of CrO_3 with F_2 at elevated temperature and pressure in a Monel reactor with a water-cooled lid. This method requires careful temperature control. The recommended conditions are 140 °C with yields of 25% of CrF_4O and 75% of CrO_2F_2. If the reaction temperature is increased, the yield of CrF_4O increases, but CrF_5 is obtained as a byproduct, which is very difficult to separate from CrF_4O.[5] It thus appears that the advantage of the previous method[2,5] of more readily available starting materials (CrO_3 + F_2 vs. CrO_2F_2 + KrF_2) is mitigated by lower yields, more complex hardware requirements, and more difficult product purification.

Properties. CrF_4O was identified by its vapor pressure, melting point (55 °C),[2] and vibrational spectra (see below). It is highly soluble in BrF_5, SO_2ClF, and anhydrous HF. The ^{19}F NMR spectrum of CrF_4O in BrF_5 at −40 °C shows a broad singlet (~100 Hz) at 488 ppm and in SO_2ClF between −10 and −120

---

(5) Hope, E. G.; Jones, P. J.; Levason, W.; Ogden, J. S.; Tajik, M.; Turff, J. W. *J. Chem. Soc., Dalton Trans.* **1985**, 529.

(6) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(7) Miller, F. A.; Harney, B. M. *Appl. Spectrosc.* **1969**, *23*, 8.

(8) Christe, K. O. *Inorg. Chem.* **1973**, *12*, 1580.

(9) Green, P. J.; Gard, G. L. *Inorg. Chem.* **1977**, *16*, 1243.

(10) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(11) Slivnik, J.; Smalc, A.; Lutar, K.; Zemva, B.; Frlec, B. *J. Fluorine Chem.* **1975**, *5*, 273.

(12) Bougon, R.; Bui Huy, T.; Lance, M.; Abazli, H. *Inorg. Chem.* **1984**, *23*, 3667.

Table I. Vibrational Spectra (cm^{-1}) of Monomeric and Polymeric CrF_4O Compared to Those of MoF_4O

CrF_4O							MoF_4O				
	monomer			polymer				polymer			
				IR solid					RA solid[c]		
RA, HF soln	RA, BrF_5 soln	IR, matrix	IR, gas (C_{4v})	+30 °C	−267 °C	RA solid −140 °C	monomer IR gas[a]	IR solid[b]			RA melt[c]
1008 w, br	1027 m, p	1028	1028 m ($\nu_1(A_1)$)	998 s	996 s	999 ms	1049 (ν_1)	1035 s	1039 s	1042 s	
			828 vw			789 mw		735 sh		740 m	
						718 sh		715 m	716 mw	721 mw	
		746, 742	755 vs ($\nu_7(E)$)	709 vs	725 vs, br	704 s	721 vs (ν_7)	700 vs	706 s		712 s, p
677 vs	d	686	695 ms ($\nu_2(A_1)$)			692 ms	(721) (ν_2)	690 sh	692 vw, sh		
				665 ms	660 ms	666 mw					
590–570 w, vbr						650 vs		665 s	661 m	668 s	665 m, p
										571 w	
				530 m	525 m	528 vw		538 m	530 vw	529 w	
						517 vvw		508 m	506 vw	506 vw	
						377 w			334 w, sh	333 m	
									316 mw		
					336 m	350 mw			308 mw	309 ms	310 m
345 w	340 mw, dp	320	($\nu_8(E)$)							275 w	
		277	($\nu_9(E)$)		299 w	293 w			258 m		244 vw, br
	269 w, p	271	($\nu_3(A_1)$)		289 mw	273 w			244 w, sh	222 m	
					264 ms	260 sh				216 vw, sh	
						188 vw			172 w		
									122 w		

[a] Reference 13. [b] Approximate frequencies from ref 3. [c] Reference 19; for the solid two different spectra were obtained depending on whether the sample had been prepared by sublimation or by solidification of the melt. [d] Obscured by BrF_5 solvent band.

°C a narrow singlet (~20 Hz) at about 485 ppm downfield from external $CFCl_3$. This suggests that all four fluorines are equivalent as expected for a monomeric, square-pyramidal CrF_4O molecule. This was also confirmed by Raman spectroscopy (see below). CrF_4O is stable in passivated steel, Teflon, or flamed-out quartz but not in Pyrex.

Vibrational Spectra and Structure. The square-pyramidal tetrafluoride oxides of Mo, W, and Re are rare exceptions[13] to the Gillespie–Nyholm valence shell electron pair repulsion (VSEPR) theory,[14] which predicts for pentacoordinated XF_4O molecules C_{2v} symmetry, i.e. a trigonal-bipyramidal structure. Whereas the square-pyramidal structures of monomeric WF_4O and MoF_4O are well-established by electron diffraction studies,[15,16] the only previous evidence for CrF_4O having an analogous C_{4v} structure was based on a recent infrared matrix isolation study.[5] The results of our study confirm the previous matrix data[5] and provide additional data on the infrared spectrum of the gas, the Raman spectra of its solutions, and the infrared and Raman spectra of solid, polymeric CrF_4O.

We were in the process of studying the infrared spectra of CrF_4O in nitrogen and neon matrices when we learned of the independent work at the University of Southampton.[5] Since our data for the N_2 matrices were in excellent agreement with the results of the Southampton group, we discontinued that part of our study. Our results for the neon matrices raise, however, one minor question concerning the splitting of $\nu_7(E)$ into two components in the N_2 matrix. This splitting has been attributed to a matrix site effect.[5] Since in the neon matrix a similar splitting is observed for ν_7, alternate explanations might have to be considered.

The infrared spectra of gaseous CrF_4O (see Figures 1 and 2 and Table I) provide further evidence for a monomeric CrF_4O molecule of symmetry C_{4v}. A six-atom XF_4O molecule of symmetry C_{4v} has nine fundamental vibrations, which are classified as $3\ A_1 + 2\ B_1 + B_2 + 3\ E$, of which only the A_1 and the E modes are infrared active. Of the six infrared-active modes, three are stretching vibrations and are the only ones expected to occur above the cutoff frequency of the AgCl windows used. As can be seen from Figure 1, three bands were observed and their frequencies are in good agreement with the matrix data.[5] Additional evidence for the C_{4v} structure comes from the observed band contours (see

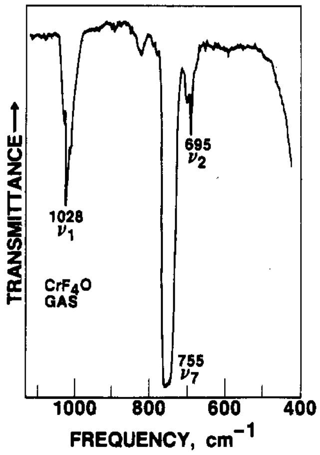


Figure 1. Infrared spectrum of gaseous CrF_4O at 13 torr in a 5-cm Teflon cell with AgCl windows.

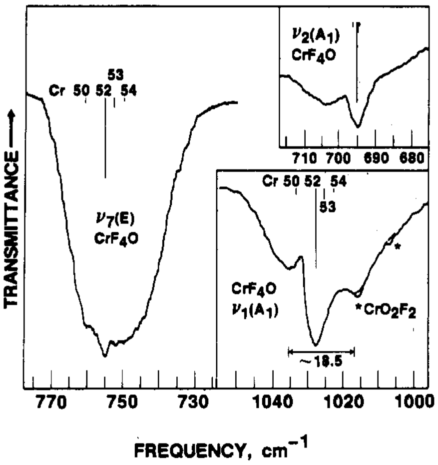


Figure 2. Infrared band contours of ν_7, ν_2, and ν_1 of gaseous CrF_4O at 13 torr. The $^{50-54}Cr$ bars indicate the relative abundance and splittings of the chromium isotopes, as observed in matrix-isolated CrF_4O. The band contour of ν_1 is slightly distorted by the presence of a trace of CrO_2F_2 (*).

---

(13) Paine, R. T.; McDowell, R. S. *Inorg. Chem.* **1974**, *13*, 2366.
(14) Gillespie, R. J. *Molecular Geometry*; Van Nostrand-Reinhold: London, 1972.
(15) Robiette, A. G.; Hedberg, K.; Hedberg, L. *J. Mol. Struct.* **1977**, *37*, 105.
(16) Iijima, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 373.

Figure 2). Although these contours are complicated by the presence of four chromium isotopes (^{50}Cr, 4.5%; ^{52}Cr, 83.8%; ^{53}Cr, 9.4%; ^{54}Cr, 2.3%), the PR branch splittings of about 18–19 cm^{-1} for the A_1 parallel bands and of about 12 cm^{-1} for the perpendicular band of species E are in good agreement with a previous analysis for square-pyramidal MoF_4O, WF_4O, and ReF_4O.[13] In all infrared spectra of gaseous CrF_4O we have observed a weak infrared band at 826 cm^{-1} of constant relative intensity. This band is probably due to a combination band or overtone of CrF_4O but at the present time cannot positively be assigned.

Since CrF_4O is highly soluble in both BrF_5 and HF, it was possible to obtain partial Raman spectra for solutions. In agreement with the ^{19}F NMR data (see above), the Raman data (see Table I) suggest that CrF_4O is monomeric in BrF_5 solution. Within experimental error the Cr=O stretching frequency for the BrF_5 solution is identical with those of the gas and the matrix-isolated species. Although the symmetric CrF_4 stretching mode, $\nu_2(A_1)$, was obscured by an intense BrF_5 band, two deformation modes were observable at 340 and 269 cm^{-1}. The latter was polarized, thus confirming its assignment to the symmetric CrF_4 deformation mode, $\nu_3(A_1)$, as previously proposed.[5]

For the HF solution of CrF_4O, a relatively broad band at 1008 cm^{-1} and a very intense band at 677 cm^{-1} were observed in the Cr=O and Cr—F stretching mode regions, respectively. Their frequencies are intermediate between those of monomeric CrF_4O (see Table I) and CrF_5O^- (see below). Therefore, it is not unreasonable to attribute these observed bands to a polyanion such as $Cr_2F_9O_2^-$ formed according to

$$2CrF_4O + 2HF \rightleftarrows H_2F^+ + Cr_2F_9O_2^-$$

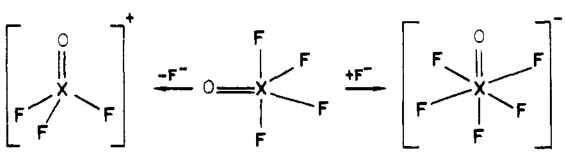
This interpretation is in accord with previous results obtained for the $HF-MoF_4O$ and $HF-WF_4O$ systems[17] and is further supported by the observation of a broad weak Raman band at about 580 cm^{-1}, similar to that observed at 576 cm^{-1} for $Mo_2F_9O_2^-$.[18]

The ^{19}F NMR spectrum of the HF solution of CrF_4O at −30 °C was also recorded and showed in addition to the HF signal at ϕ −199 a very broad unresolved signal at ϕ 467. The upfield shift of 21 ppm relative to monomeric CrF_4O in BrF_5 (see above) parallels that previously observed for WF_4O and $W_2F_9O_2^-$.[17]

The infrared and Raman spectra of solid CrF_4O are shown in Figure 3. A comparison of the observed spectra to those of solid MoF_4O[19] (see Table I) shows close similarities, indicating similar structures for the two compounds, i.e. endless cis-fluorine-bridged chains of XF_5O pseudooctahedrons.[3] For solid MoF_4O, two slightly different Raman spectra have been reported[19] for sublimed MoF_4O and the solidified melt, respectively (see Table I). Although CrF_4O is known[2] to undergo a solid–solid phase transition at 24 °C, the Raman spectra of sublimed CrF_4O and of the solidified melt were found to be identical within experimental error. It appears that the polymorphism observed for both MoF_4O and CrF_4O may involve only slightly different packings of the chains and that the packings in MoF_4O may differ from those in CrF_4O, as indicated by the fact that sublimed MoF_4O[3] and CrF_4O[1] have vastly different unit cells and X-ray powder patterns.

Amphoteric Nature. By analogy with MoF_4O[16] and WF_4O[15] and on the basis of its vibrational spectra (see above), monomeric CrF_4O has a square-pyramidal structure of symmetry C_{4v}. This square-pyramidal-type structure differs only very little in energy from that of the more common trigonal bipyramid.[14] Since trigonal-bipyramidal molecules generally exhibit a very pronounced tendency to form both tetrahedral cations and octahedral anions[20] it was interesting to explore whether square-pyramidal molecules, such as CrF_4O, exhibit a similarly strong amphoteric character. It was found that CrF_4O is a very strong Lewis acid, capable of forming a stable NO^+ salt with FNO:

$$FNO + CrF_4O \rightarrow NO^+CrF_5O^-$$



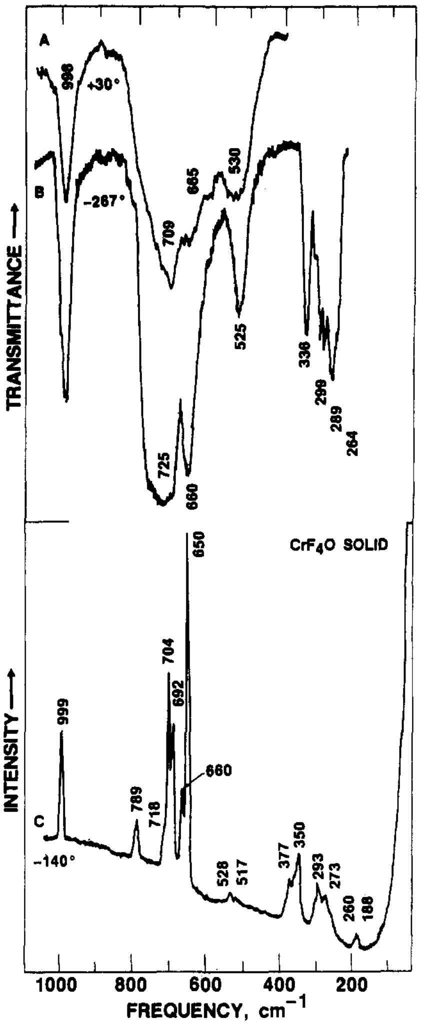


Figure 3. Vibrational spectra of solid CrF_4O: (A) infrared spectrum of the solid between AgCl disks at room temperature; (B) infrared spectrum of the solid at 6 K on a CsI window; (C) Raman spectrum of the solid in a quartz tube recorded at −140 °C with 647.1-nm excitation.

On the basis of its DSC, $NO^+CrF_5O^-$ starts to decompose exothermically at about 237 °C with formation of the polyanion salt $NO^+CrF_5O^- \cdot nCrF_4O$, which was characterized by its infrared spectrum (see below).

The Lewis basicity of CrF_4O was also studied. With AsF_5, it does not form a stable adduct at temperatures as low as −78 °C. This indicates that CrF_4O is a rather weak Lewis base. A similar behavior has previously been found for MoF_4O, WF_4O, and ReF_4O. For example, MoF_4O and WF_4O form with the strong Lewis acid SbF_5 only marginally stable 1:1 adducts that consist of either fluorine-bridged zigzag chains ($MoF_4O \cdot SbF_5$) or dimers containing eight-membered rings with two Re, two Sb, and four F atoms ($ReF_4O \cdot SbF_5$).[21] It therefore appears that all these square-pyramidal molecules are strong fluoride ion acceptors (Lewis acids) but relatively weak F^- donors (Lewis bases).

$NO^+CrF_5O^-$. Synthesis and Properties. CrF_4O combines with FNO in a 1:1 mole ratio to yield the solid adduct $NO^+CrF_5O^-$. The compound is a stable, crystalline, pink solid. Its ionic nature

---

(17) Bougon, R.; Bui Huy, T.; Charpin, P. *Inorg. Chem.* **1975**, *14*, 1822.

(18) Beuter, A.; Sawodny, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1020.

(19) Beattie, I. R.; Livingston, K. M. S.; Reynolds, D. J.; Ozin, G. A. *J. Chem. Soc. A* **1970**, 1210.

(20) Christe, K. O.; Schack, C. J.; Pilipovich, D. *Inorg. Chem.* **1972**, *11*, 2205.

(21) Fawcett, J.; Holloway, J. H.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1981**, 1212.

Table II. Vibrational Spectra (cm^{-1}) of CrF_5O^- Compared to Those of MoF_5O^- and WF_5O^-

assignt in point group C_{4v}	approx descripn of mode	$NO^+CrF_5O^-$		$NO^+MoF_5O^-$ [a]		$Cs^+MoF_5O^-$ [b]		$NO^+WF_5O^-$ [a]		$Cs^+WF_5O^-$ [b]	
		IR (25 °C)	RA (−140 °C)	IR	RA	IR	RA	IR	RA	IR	RA
$\nu_1(A_1)$	$\nu(XO)$	980 s	993 vs	990 s	985 (10)	973 vs	973 vs	1003 s	1001 (10)	987 vs	989 vs
$\nu_2(A_1)$	$\nu_s(XF_4)$		613 s		665 (7.2)	662 vw	666 m	680 sh	684 (3.5)	686 w	689 m
$\nu_3(A_1)$	$\nu(XF')$	520 sh	530 sh	436 ms		492 m		455 ms		507 m	
$\nu_4(A_1)$	$\delta_s(XF_4)$		302 m		293 (1)	300 w			292 sh	286 m	287 vw
$\nu_5(B_1)$	$\nu_s(XF_4)$		577 m		557 (0.6)		(580)		591 (0.4)		594 vw
$\nu_6(B_1)$	$\delta(XF_4)$										
$\nu_7(B_2)$	$\delta_{sciss}(XF_4)$										
$\nu_8(E)$	$\nu_{as}(XF_4)$	586 vs, br		650 vs, br		605 vs		610 vs, br		608 vs	
$\nu_9(E)$	$\delta(OXF_4)$	330 m	346 mw		317 (6.2)		324 m		327 (5.9)	329 s	331 m
$\nu_{10}(E)$	$\delta(F'XF_4)$	279 m	277 m			252 s				242 s	
$\nu_{11}(E)$	$\delta_{as}(XF_4)$										

[a] Reference 17. [b] Reference 22.

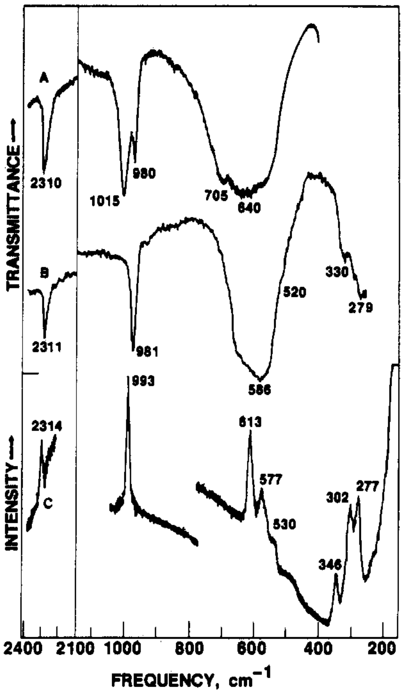


Figure 4. Vibrational spectra of solid $NO^+CrF_5O^-$: (A) infrared spectrum of a mixture of $NO^+CrF_5O^-$ and $NO^+CrF_5O^-{\cdot}nCrF_4O$ between AgCl disks at room temperature; (B) infrared spectrum of $NO^+CrF_5O^-$; (C) Raman spectrum of solid $NO^+CrF_5O^-$ in a glass capillary recorded at −140 °C with 647.1-nm excitation.

was established by infrared and Raman spectroscopy (see Figure 4 and Table II), which shows the characteristic NO^+ stretching mode at about 2310 cm^{-1}.[17] The assignments for CrF_5O^- in point group C_{4v} were made by analogy with those previously reported[17,22] for MoF_5O^- and WF_5O^- (see Table II) and show plausible trends if the corresponding mass and coupling effects are taken into consideration. Of the given assignments, those for ν_1, ν_2, and ν_8 are firm while those for ν_3, ν_4, ν_5, ν_9, and ν_{10} are somewhat tentative.

A comparison of the vibrational spectra of $NO^+CrF_5O^-$ with the two previously reported infrared bands[5] for $Cs^+CrF_5O^-$ shows substantial frequency differences. The drop in the Cr=O stretching frequency by 25 cm^{-1} from $NO^+CrF_5O^-$ (980 cm^{-1}) to $Cs^+CrF_5O^-$ (955 cm^{-1}) is larger but similar to those previously found[17,22] for the corresponding NO^+–Cs^+ couples of MoF_5O^- and WF_5O^- and most likely is caused to some extent by the different degree of anion–cation interactions. The large frequency increase of about 100 cm^{-1} for the antisymmetric CrF_4 stretching mode from $NO^+CrF_5O^-$ to $Cs^+CrF_5O^-$ is more difficult to explain. This band is generally very broad, and the choice of the band center can be difficult. However, in this case the shift is opposite to that reported for the $NO^+MoF_5^-$ and $Cs^+MoF_5O^-$ couple, and the reported $Cs^+CrF_5O^-$ value (650–720 cm^{-1}) is outside the range (550–650 cm^{-1}) of this band in $NO^+CrF_5O^-$ but falls within the range observed for the polyanion $CrF_5O^-{\cdot}nCrF_4O$ (see below). A comparison of the data of Table II shows that for the NO^+ and Cs^+ salts of MoF_5O^- and WF_5O^- there are also some large frequency shifts for the bands assigned to the X–F′ stretching mode $\nu_3(A_1)$.[17,22] At this time it is difficult to say to what extent these shifts are for real.

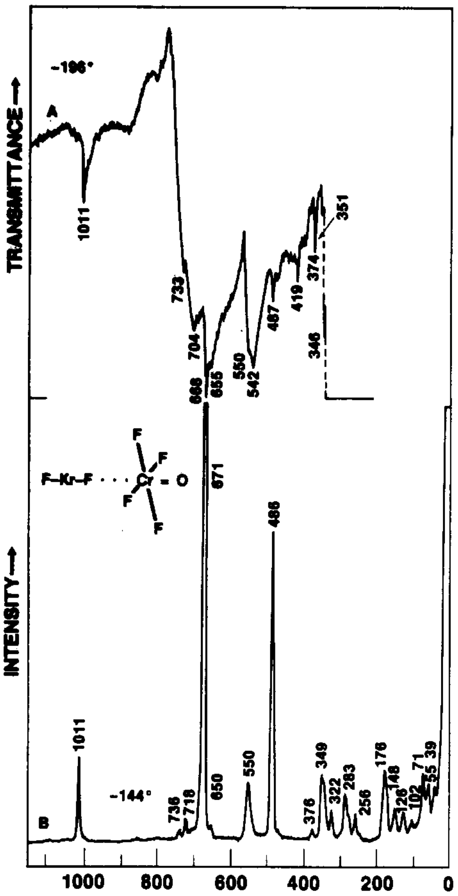


Figure 5. Vibrational spectra of solid $KrF_2{\cdot}CrF_4O$: (A) infrared spectrum of the solid between AgCl disks at −196 °C (broken line indicates absorption due to the AgCl window material); (B) Raman spectrum of the solid in a quartz capillary recorded at −144 °C with 647.1-nm excitation.

The infrared spectrum of a mixture of $NO^+CrF_5O^-$ and $NO^+CrF_5O^-{\cdot}nCrF_4O$ obtained by controlled pyrolysis of NO^+-CrF_5O^- in a DSC cell is shown as trace A in Figure 4. Compared to that of $NO^+CrF_5O^-$ the spectrum shows the expected changes; i.e., both the Cr–O and Cr–F stretching modes are shifted toward higher frequencies, which are intermediate between those of CrF_5O^- and solid CrF_4O. These data indicate that salts such as

---

(22) Beuter, A.; Sawodny, W. *Z. Anorg. Allg. Chem.* **1976**, *427*, 37.

Table III. Vibrational Spectra (cm^{-1}) and Relative Intensities[a] of Solid $KrF_2{\cdot}CrF_4O$ Compared to Those of KrF_2, $KrF_2{\cdot}MoF_4O$, and $KrF_2{\cdot}WF_4O$

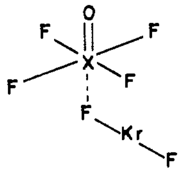
KrF_2[b]		$KrF_2{\cdot}CrF_4O$		$KrF_2{\cdot}MoF_4O$[c]	$KrF_2{\cdot}WF_4O$[c]	
IR (gas)	RA (gas, solid)	IR (−196 °C)	RA (−144 °C)	RA	RA	assignt
		1011 m	1011 (1.1)	1034 (1.2), 1025 (3.3)	1041 (0.8), 1034 (4.5)	$\nu(X{=}O)$
		733 w	736 (0.05)	702 (0.5)		
		704 s	718 (0.2)	698 (0.7)	712 (0.4)	
		668 s	671 (10)	691 (6.3)	706 (1.8)	$\nu_s(XF_4)$ (in phase)
		655 vs	650 (0.1)	661 (0.2)		$\nu_{as}(XF_4)$
			550 (0.7)	582 (1.6)	611 (0.3)	$\nu_s(XF_4)$ (out of phase)
		550 sh	550 (0.7)	579 (5.3)	581 (4.5)	$\nu(Kr{-}F_t)$[d] or $\nu_{as}(KrF_2)$
588 vs	...	542 vs		566 (10)	571 (10)	
					504 (0.4)	
	462 (s) (10)	487 w	486 (4.1)	479 (4.0)	469 (1.7)	$\nu(Kr{-}F_b)$[d] or $\nu_s(KrF_2)$
	449 (g) (10)			462 (5.9)	450 (4.2)	
		419 w				$\nu(F_b{\cdots}Cr)$[d]
		374 w	376 (0.1)			
		351, 341 w	349 (0.8)	312 (3.6)	312 (1.6)	$\delta(OXF_4)$
			322 (0.3)	303 (1.5)	301 (1.2)	$\delta_s(XF_4)$ (out of phase)
			283 (0.5)	260 (0.01)		$\delta_{sciss}(XF_4)$
				266 (0.7)	221 (0.4)	$\delta_{as}(XF_4)$ (in plane)
			256 (0.2)	220 sh		
				210 (0.4)	206 (0.2)	
233	...		176 (0.9)	170 (2.0)	172 (1.8)	π, $\delta(F_t{-}Kr{-}F_b)$
			148 (0.3)	155 (0.8)	158 (0.6)	$\delta(F_b{\cdots}XF_4O)$
				140 (0.8)	144 (0.8)	
				130 (0.6)	132 (0.7)	lattice modes
				116 (0.2)	115 (0.3)	
			126 (0.3)	79 (1.7)	78 (1.0)	
			102 (0.1)	72 (1.5)	68 (1.2)	
				60 (0.5)		
			71 (0.6)	52 (3.0)		
			55 (0.2)	37 (1.2)		
			39 (0.1)	29 (0.6)		

[a] Relative RA intensities based on peak heights and not peak areas. [b] Reference 24. [c] Reference 23. [d] F_t = terminal fluorine; F_b = bridging fluorine.

$NO^+Cr_2F_9O_2^-$ exist and are thermally more stable than $NO^+CrF_5O^-$.

$KrF_2{\cdot}CrF_4O$. During preparations of CrF_4O from CrO_2F_2 and an excess of KrF_2 it was noticed that KrF_2 was not only unable to replace the second oxygen of CrO_2F_2 by two fluorines but also formed a $CrF_4O{\cdot}KrF_2$ adduct. This adduct formation rendered the removal of the excess KrF_2 quite difficult. The adduct was found to be a purple solid that at room temperature reversibly dissociates to KrF_2 and CrF_4O. The formation of a $KrF_2{\cdot}CrF_4O$ adduct is not surprising in view of the fact that both WF_4O and MoF_4O form adducts with KrF_2.[23] The nature of $KrF_2{\cdot}CrF_4O$ was established by low-temperature infrared, Raman, and ^{19}F NMR spectroscopy.

Vibrational Spectra. The low-temperature infrared and Raman spectra of $KrF_2{\cdot}CrF_4O$ were recorded and are shown in Figure 5. The observed frequencies are summarized in Table III. The structural identification of this adduct was facilitated by the fact that the analogous $KrF_2{\cdot}MoF_4O$ and $KrF_2{\cdot}WF_4O$ adducts had previously been thoroughly characterized by Holloway and Schrobilgen.[23] These investigators have established by nuclear magnetic resonance and vibrational spectroscopy that these adducts are predominantly covalent, containing a Kr–F–metal bridge in a position trans to the oxygen ligand:



A comparison of the vibrational spectra of $KrF_2{\cdot}CrF_4O$ with those of $KrF_2{\cdot}MoF_4O$ and $KrF_2{\cdot}WF_4O$[23] and KrF_2[24] (see Table III) shows smooth trends for this series and the absence of the bands characteristic for either KrF^+[25,26] and CrF_5O^- (see above) or free KrF_2[24] and CrF_4O (see above). This is convincing proof that $KrF_2{\cdot}CrF_4O$ must also be considered as a predominantly covalent adduct with a Kr–F–X bridge. From the relative Raman intensities of the CrF stretching modes it can furthermore be concluded that the CrF_4O part of the adduct must be highly symmetrical, i.e. that the fluorine bridge must be trans to the oxygen atom. The assignments for $KrF_2{\cdot}CrF_4O$ are given in Table III and were made by analogy to those[23] of $KrF_2{\cdot}MoF_4O$ and $KrF_2{\cdot}WF_4O$. When the spectra of this series are compared, three points must be kept in mind: (i) as one goes from CrF_4O to WF_4O the relative Raman intensities of the XF_4 modes decrease due to an increasing $X^{\delta+}{-}F^{\delta-}$ polarity of the X–F bonds; (ii) the relative Raman intensities given in Table III are peak heights and not peak areas, which can lead to the false impression that, for example, the 579- and 566-cm^{-1} bands (derived from ν_{as} of KrF_2) in $KrF_2{\cdot}MoF_4O$ are more intense than the much broader bands at 462 and 479 cm^{-1} (derived from ν_s of KrF_2); (iii) the $KrF_2{\cdot}CrF_4O$ adduct does not show a doubling of some of the bands, indicating either a different unit cell or less coupling between the molecules within a unit cell for $KrF_2{\cdot}CrF_4O$.

Table IV. Frequencies (cm^{-1}) of the KrF_2 Stretching Modes in KrF_2 Adducts

	$KrF^+SbF_6^-$[a]	$KrF_2{\cdot}WF_4O$[b]	$KrF_2{\cdot}MoF_4O$[b]	$KrF_2{\cdot}CrF_4O$
$\nu(F_t{-}Kr)$	619, 615	581, 571	579, 566	550
$\nu(Kr{\cdots}F_b)$	338	469, 450	479, 462	486

[a] Reference 25. [b] Reference 23.

The frequencies of the stretching modes of the KrF_2 part of the $KrF_2{\cdot}XF_4O$ adducts can be used as a qualitative measure for the ionic character of the adduct.[23] With increasing ionicity, the frequency separation between $\nu_{as}(KrF_2)$ or $\nu(KrF_t^+)$ and $\nu_s(KrF_2)$ or $\nu(Kr{\cdots}F_b)$ increases. As can be seen from Table IV, Kr-

---

(23) Holloway, J. H.; Schrobilgen, G. J. *Inorg. Chem.* **1981**, *20*, 3363.
(24) Claassen, H. H.; Goodman, G. L.; Malm, J. G.; Schreiner, F. *J. Chem. Phys.* **1965**, *42*, 1229.
(25) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1976**, *15*, 22.
(26) Frlec, B.; Holloway, J. H. *Inorg. Chem.* **1976**, *15*, 1263.

F_2·CrF_4O exhibits the smallest frequency separation, suggesting that the covalency of the KrF_2·XF_4O adducts increases on going from X = W to X = Cr.

^{19}F NMR Spectra. The increase in covalency for KrF_2·CrF_4O was further supported by ^{19}F NMR spectroscopy. Whereas KrF_2·XF_4O (X = Mo, W) show unequivocal NMR evidence for a fluorine-bridged adduct in SO_2ClF solution,[23] the corresponding KrF_2·CrF_4O adduct in SO_2ClF showed in the temperature range −120 to −10 °C only two sharp signals due to CrF_4O and KrF_2 without any sign of coupling. The chemical shift of the CrF_4O resonance exhibited relatively little temperature dependence and occurred in the range 482–486 ppm. However, the chemical shift of KrF_2 showed a very pronounced temperature dependence varying from about 63 ppm at −118 °C to about 82 ppm at −10 °C. A similarly pronounced temperature dependence of the chemical shift of KrF_2 has previously been observed for BrF_5 solutions (68 ppm at −150 °C and 78 ppm at 27 °C) and was attributed to solvation effects.[25]

Conclusion. The structure and physical and chemical properties of CrF_4O resemble those of WF_4O and MoF_4O. Thus, CrF_4O is also a strong Lewis acid and forms a stable $NO^+CrF_5O^-$ salt. With KrF_2 it forms an unstable, highly covalent 1:1 adduct which in SO_2ClF solution, contrary to those of WF_4O and MoF_4O, is completely dissociated to KrF_2 and CrF_4O. The major difference between CrF_4O and MoF_4O and WF_4O is the strong increase in oxidizing power from WF_4O to CrF_4O with the latter being capable of oxidizing O_2 to O_2^+ and NF_3 to NF_4^+.[27]

Acknowledgment. We are grateful to Drs. C. J. Schack and L. R. Grant and R. D. Wilson for their help and to the U.S. Army Research Office and the Office of Naval Research for financial support. R.A.B. is also indebted to Dr. W. Kaska and the University of California, Santa Barbara, CA, for their hospitality and to the DRET for financial support.

Registry No. CrF_4O, 23276-90-6; CrO_2F_2, 7788-96-7; HF, 7664-39-3; $NO^+CrF_5O^-$, 102110-04-3; AsF_5, 7784-36-3; CrF_3O, 43997-25-7; KrF_2·CrF_4O, 102110-05-4.

---

[27] Christe, K. O.; Wilson, W. W., unpublished data.

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of Electron Transfer to Transition-Metal Complexes by Photochemically Produced Tris(bipyridyl)ruthenium(1+) Ion[1]

Philip Connolly, James H. Espenson,* and Andreja Bakac

Received October 29, 1985

Rate constants were determined for the one-electron reduction of $Cr(H_2O)_6^{3+}$, several organochromium cations of the family $(H_2O)_5CrR^{2+}$, several substituted pyridine complexes in the series $(H_2O)_5CrNC_5H_4X^{3+}$, cobalt(III) amine complexes, and miscellaneous species including Yb_{aq}^{3+} and (1*R*,4*R*,8*S*,11*S*)-Ni(tmc)$^{2+}$ (where tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The results are considered in light of the Marcus equation. The data for the pyridine complexes are correlated by the Hammett equation; the reaction constant in comparison with those of other complexes indicates that electron transfer occurs directly to the metal and not, as in certain other instances, by initial reduction of the pyridine ligand bound to chromium. The qualitative differences in rates can be rationalized by a simple MO scheme.

Introduction

The photochemistry of $Ru(bpy)_3^{2+}$ and the excited-state reactivity of $[Ru(bpy)_3^{2+}]^*$ have received much attention during the past decade.[2-7] The electronic structure of the excited state can be approximated most closely as a charge-separated Ru(III) metal center (a strong oxidant) and a ligand radical anion (a strong reductant).[3] Our interest here concerns the chemical reactivity of $Ru(bpy)_3^+$, the species that results from quenching the excited state with an electron donor, such as Eu_{aq}^{2+} (most frequently used here; see eq 1), $Ru(NH_3)_6^{2+}$, or $Hasc^-$ (ascorbate ion).

$$[Ru(bpy)_3^{2+}]^* + Eu_{aq}^{2+} \rightarrow Ru(bpy)_3^+ + Eu_{aq}^{3+} \qquad (1)$$

The monovalent ruthenium cation so formed contains the metal in the 2+ oxidation state and a ligand radical anion, $bpy^{\bullet-}$.[3] The use of laser flash photolysis techniques makes $Ru(bpy)_3^+$ conveniently accessible. It is an exceptionally strong reducing agent ($E°_{2+/+} = -1.28$ V)[3] and thus a particularly useful probe for complexes that are very weak electron acceptors. Their reactions with $Ru(bpy)_3^+$ have, therefore, a very large driving force and are nearly irreversible. The general reaction with such acceptors (A) is

$$Ru(bpy)_3^+ + A \rightarrow Ru(bpy)_3^{2+} + D \quad (k_2) \qquad (2)$$

The complexes investigated are very weak oxidizing agents except for a few cobalt(III) complexes that provided useful calibrations. The following classes of complexes have been investigated: (a) hydrated metal ions and other relatively simple complexes that are poor electron acceptors with well-characterized one-electron-reduced forms, including $Yb(aq)^{3+}$, $Sm(aq)^{3+}$, $Cr(H_2O)_6^{3+}$, and $Ni(tmc)^{2+}$;[8] (b) organometallic complexes, particularly in the series of $(H_2O)_5CrR^{2+}$ cations, where no previous examination has been made of their abilities to undergo one-electron reduction; (c) chromium(III) pyridine complexes, such as $(H_2O)_5CrNC_5H_5^{3+}$ and substituted analogues.[9,10] In the last

---

(1) Based on the Ph.D. thesis of P.C., Iowa State University, 1985.

(2) Demas, J. N.; Adamson, A. W. *J. Am. Chem. Soc.* **1973**, *95*, 5159.

(3) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No. 168*, 1.

(4) Leopold, K. R.; Haim, A. *Inorg. Chem.* **1978**, *17*, 1753.

(5) Jonah, C. D.; Matheson, M. S.; Meisel, D. *J. Am. Chem. Soc.* **1978**, *100*, 1449.

(6) Creutz, C.; Chou, M.; Netzel, T. L.; Okumura, M.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 1309.

(7) Kurimura, Y.; Endo, E. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3835.

(8) tmc (= "tetramethylcyclam" or $Me_4N[14]aneN_4$) = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane. [Note the corrected (compared to usage in some of the literature) chirality designators for this nickel complex, often referred to as the "trans III" isomer (Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 713).] Under the reaction conditions the nickel(II) complex is a mixture of aquo and hydroxo species (pK_a = 11.93: Herron, N.; Moore, P. *Inorg. Chim. Acta* **1979**, *36*, 89).

0020-1669/86/1325-2169$01.50/0